

2

AD-A232 827

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 58

Template Synthesis of Metal Microtubules

by

Charles L. Brumlik and Charles R. Martin
Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

Prepared for publication

in

Journal of American Chemical Society

March 12, 1991

Reproduction in whole or part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

*This statement should also appear in Item 10 of Document
Control Data - DD Form 1473. Copies of form
Available from cognizant contract administrator

DTIC FILE COPY

DTIC
ELECTE
MAR 27 1991
S D

91 3 20 008

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT APPROVED FOR PUBLIC DISTRIBUTION, DISTRIBUTION UNLIMITED.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR TECHNICAL REPORT #58			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Dr. Charles R. Martin Department of Chemistry		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Colorado State University Ft. Collins, CO 80523		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract # N00014-82K-0612		
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Template Synthesis of Metal Microtubules					
12. PERSONAL AUTHOR(S) Charles J. Brumlik and Charles R. Martin					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) (91,3,12) March 12, 1991	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>We have recently described a "template" method for the synthesis of organic microtubules. This method entails the use of the pores in a microporous membrane as templates for tubule formation. The key to the tubule-formation process is the presence of "molecular anchors" on the pore walls. These anchors insure that the tubule-forming materials deposits as a thin skin which lines the pore wall. We describe in this paper an electrochemical template method for the synthesis of metal (Au) microtubules. We also present a general paradigm for the formation of molecular anchors on the pore walls of alumina template membranes. We believe that this paradigm should allow for the synthesis of microtubules composed of any desired material.</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

TEMPLATE SYNTHESIS OF METAL MICROTUBULES

Charles J. Brumlik and Charles R. Martin*

Department of Chemistry

Colorado State University

Fort Collins, CO 80523

Abstract. We have recently described a "template" method for the synthesis of organic microtubules. This method entails the use of the pores in a microporous membrane as templates for tubule formation. The key to the tubule-formation process is the presence of "molecular anchors" on the pore walls. These anchors insure that the tubule-forming material deposits as a thin skin which lines the pore wall. We describe in this paper an electrochemical template method for the synthesis of metal (Au) microtubules. We also present a general paradigm for the formation of molecular anchors on the pore walls of alumina template membranes. We believe that this paradigm should allow for the synthesis of microtubules composed of any desired material.



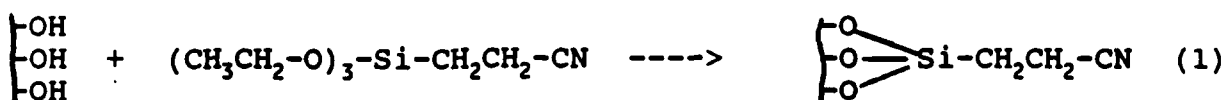
*To whom correspondence should be addressed.

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Availability / or Special
A-1	

Organic microtubules have recently caused a great deal of excitement in the chemistry, physics, and materials science communities (1). We have developed a novel "template" method for synthesizing such tubules (1c). This method entails using the pores in a microporous membrane as templates for tubule formation. We have used this method to prepare microtubules composed of various heterocyclic polymers (1c). It seems likely that the template method could be used to synthesize microtubules composed of other materials; metals are an obvious choice. We describe, in this paper, an electrochemical template synthesis of gold microtubules (2).

In general, the template method entails synthesis of a material within the pores of a microporous membrane (1c-3). Either solid fibrils (3b) or hollow tubules (1c,2) will be obtained. Tubules will only be obtained if "molecular anchors" are present on the pore wall; these anchors assure that the material forms as a thin "skin" which lines the pore wall (1c). The challenges in synthesizing metal microtubules, then, are 1) To identify chemistry for forming the metal within the pores of the membrane, 2) To identify a suitable molecular anchor, and 3) To develop chemistry for attaching this anchor to the pore walls in the membrane. Numbers 2 and 3, above, are by far the most challenging problems. A general paradigm for solving these problems is presented in this paper.

Gold microtubules were prepared by electrochemically depositing Au into the pores of microporous alumina (Anopore, Anotech Ltd.) (3b) membranes. These membranes have 200 nm diameter pores and enormous pore densities (3b). A commercial Au plating solution (Orotemp 24, Technics) was employed. We chose an organocyanide (2-cyanoethyltriethoxysilane) as the molecular anchor to bind the electrochemically-deposited Au to the walls of the template membrane. Soriaga et al. have shown that organocyanides strongly chemisorb to Au (4). This molecular anchor was attached to the pore wall via (5)



where the -OH's represent hydroxyl groups on the pore wall.

A schematic representation of the procedure used to synthesize the Au microtubules is shown in Figure 1. A 50 nm layer of Au was first sputter-deposited, from an Ar plasma, onto one face of the silane-treated Anopore membrane. This layer was too thin to block the pores in the Anopore membrane but converted the surface of the membrane into an electrode (Figure 1A). The electrochemical cell consisted of this Au/Anopore cathode and a large-area platinized niobium mesh (Technics) anode; the anode faced the Au-coated side of the membrane. Au was deposited galvanostatically at current densities of 0.5 to 2.0 mA cm⁻²; 0.5 to 4.0 coul. cm⁻² were passed.

As indicated in Figure 1B, Au is deposited on the surface of the Anopore membrane and along the walls of the pores in this

membrane. The gold deposited along the walls forms the Au microtubules. Deposition along the walls continues (i.e. the microtubules grow longer) until the pores become completely blocked by the Au surface layer (Figure 1C); at this point, the rate of tubule growth decreases markedly. To date, we have obtained Au microtubules which are as long as 2 μm .

After tubule synthesis, the Anopore membrane can be dissolved away (6), to expose the Au microtubules. An upright ensemble of microtubules connected via a common Au base layer is obtained (Figure 1D). An electron micrograph of such an ensemble is shown in Figure 2A. The organocyanide molecular anchor is essential to this tubule formation process. If the electrochemistry illustrated in Figure 1 is conducted at an underivatized Anopore membrane, solid Au fibrils (Figure 2B) are obtained. We are currently exploring the mechanism of this novel tubule formation process.

It is not clear from Figure 2B how far down their lengths the tubules remain hollow. We have conducted several experiments which address this issue. First, electron micrographs of tubules which were broken near the base (i.e. near the Au surface layer) show that the tubules are hollow to within several hundred nm of the base. Second, while solution will not flow through the membrane when the Au surface layer is intact (i.e. Figure 1C), dissolution of the Au layer, in aqua regia, allows for solution flow through the tubule-impregnated membrane. Finally, electron micrographs of the membrane after dissolution of the Au surface

layer show that the exposed bases of the tubules are hollow. It is worth noting that dissolution of the Au base layer disconnects the tubules from each other. If the Anopore membrane is then dissolved (6), the isolated fibrils can be collected by filtration (3).

The silanization chemistry illustrated in Equation 1 provides a very general method for attaching many different types of molecular anchors to the Anopore (alumina) pore walls (5). Furthermore, a vast array of silane derivatives is available through commercial sources. Thus, as indicated earlier, we view the procedures outlined above as a general paradigm for synthesis of microtubules composed of any desired material. For example, tubules composed of a vinyl polymer might be synthesized by attaching a silane which contains an active vinyl group to the pore walls, and tubules composed of an ionic polymer might be synthesized by attaching a silane which contains a counterionic group to the pore walls. We are currently using this paradigm to synthesize microtubules composed of a variety of different materials.

Acknowledgements. This work was supported by the Office of Naval Research.

REFERENCES AND NOTES

- (1) (a) Pool, R. Science, 1990, 247, 1410. (b) Georger, J.H.; Singh, A.; Price, R.P.; Schnur, J.M.; Yager, P.; Schoen, P.E. J. Am. Chem. Soc. 1987, 109, 6169. (c) Martin, C.R.; Van Dyke, L.S.; Cai, Z.; Liang, W. J. Am. Chem. Soc. 1990, 112, 8976.
- (2) A companion paper, by Schoen et al., describes a chemical template synthesis of such tubules. Price, R.R.; Baral, S.; Schoen, P.E. J. Am. Chem. Soc. Submitted.
- (3) (a) Cai, Z.; Martin, C.R. J. Am. Chem. Soc. 1989, 111, 4138. (b) Liang, W.; Martin, C.R. J. Am. Chem. Soc. In press.
- (4) Brovo, B.G. Ph.D. Dissertation, Texas A&M University, 1990.
- (5) (a) Miller, C.J.; Majda, M. Anal. Chem. 1988, 60, 1168. (b) The Anopore surfaces were silanized by sonicating the membrane for 30 sec. in a 0.1 (v/v) % solution of 2-cyanoethyltriethoxysilane in anhydrous hexadecane. The membrane was removed from this solution and heated overnight at 100° C. The silane probably does not form as a monolayer but as a thin polymer film.
- (6) Van Dyke, L.S.; Martin, C.R. Langmuir, 1990, 6, 1118.